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(54) **Priming mixture containing no toxic materials, and cartridge percussion primer employing such a mixture**

(57) A priming mixture containing no toxic materials, in particular no Pb, Ba or Sb compounds, and presenting at least one primary explosive, an oxidizing agent, a reducing agent, and an inert friction agent; the oxidizing agent comprising stannic oxide SnO₂. The central-fire or rimfire percussion primer presents a casing containing the priming mixture, and, in the case of the central-fire primer, also an anvil.

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Description

The present invention relates to a priming mixture containing no toxic materials, in particular Pb, Ba and Sb compounds, and more specifically to a priming mixture of the above type comprising at least one primary explosive, an oxidizing agent, a reducing agent and, optionally, an inert friction agent and a secondary explosive. The present invention also relates to a primer for center-fire or rimfire percussion cartridges and including such a mixture.

As is known, the projectile propelling charge of a firearm is initiated by a percussion cap or primer. Until the late 50s, the priming mixture in the caps mainly comprised mercury fulminate, antimony trisulfide and potassium chlorate, but was later abandoned in favour of lead styphnate based mixtures containing barium (Ba) and antimony (Sb) compounds, which had the advantage of being slightly less toxic and, above all, of generating no reaction products reacting electrochemically with and so corroding the steel of which the firearms are made.

Increasingly strict pollution control, however, has now lowered the maximum concentration in the air of elements such as Pb, Sb, Ba to 0.1-0.5 mg/m³ (depending on the element and whether it is in the form of fumes, powder, etc.), whereas the Pb concentration, for example, of target ranges, particularly indoor with forced ventilation systems, has been found to be many times the above limit.

As a result, numerous "ecological" priming mixture compositions, i.e. containing none of the above pollutant elements, have been devised. European Patent n. 0012081 relates to a composition featuring a primary explosive - i.e. sensitive to shock and heat, and presenting a high flame propagation rate - with a negative oxygen content (diazodinitrophenol) combined with an oxidizing agent of zinc peroxide. The latter compound, however, is difficult to obtain in the pure state and is expensive, while the mixture itself would appear to be less sensitive at low temperature. US Patent n. 4.675.059 also relates to the same type of priming composition - i.e. a primary explosive, such as diazodinitrophenol, combined with an oxidizing agent - except that, in this case, the oxidizing agent comprises manganese dioxide, which cannot strictly be said to be nontoxic by being limited to a maximum permissible concentration in the air of 5 mg/m³. Finally, European Patent n. 0334725 again relates to the same type of priming mixture, but again featuring a not entirely nontoxic oxidizing agent of copper oxide, the fumes of which are limited to a concentration in the air of 0.2 mg/m³, i.e. to much the same value as for Pb, Sb and Ba. Moreover, the ballistic efficiency of all the above mixtures is not always comparable to that of traditional Pb mixtures.

It is an object of the present invention to provide a priming mixture composition which, while maintaining the ballistic efficiency of known Pb styphnate based mixtures, contains no Pb, Ba or Sb compounds, and is less toxic (in terms of the amount of pollutant powder/fumes produced in the air) as compared with most of the mixtures so far devised in lieu of traditional Pb mixtures.

According to the present invention, there is provided a priming mixture containing no toxic materials, in particular no Pb, Ba, Sb compounds, and comprising at least one primary explosive, an oxidizing agent, and at least one reducing agent; characterized in that said oxidizing agent comprises stannic oxide SnO₂.

The priming mixture according to the present invention also comprises at least one secondary explosive; at least one friction agent comprising inert abrasive powder; and a binding agent.

More specifically, the oxidizing agent comprises exclusively stannic oxide; and the priming mixture composition according to the invention may range between: 20 to 60% by weight of primary explosive; 3 to 15% by weight of secondary explosive; 20 to 40% by weight of stannic oxide; 3 to 15% by weight of reducing agents; 5 to 25% by weight of friction agents; and 1 to 5% by weight of binding agent.

The primary explosive is selected from the group comprising diazodinitrophenol, tetrazene, nitromannitol, KDNBF, and mixtures thereof; while the secondary explosive comprises pentaerythritol tetranitrate.

The friction agent is selected from the group comprising calcium silicide, silicon monoxide, glass powder, and mixtures thereof; the reducing agent is selected from the group comprising aluminium powder, titanium powder, zirconium powder, boron powder, and mixtures thereof; and the binding agent is preferably gum arabic.

The priming mixture according to the present invention has surprisingly been found to present a ballistic efficiency fully comparable to that of traditional Pb styphnate mixtures, except that it is slightly less sensitive, though fully within NATO standard limits.

On the other hand, the priming mixture according to the invention functions excellently even at low temperatures, so much so as to conform with NATO AC225 standards, and may therefore be used not only for practice or target range cartridges, like most known "ecological" primer compositions, but also for combat ammunition.

A number of non-limiting embodiments of the present invention will now be described by way of example.

EXAMPLE 1

150 gr of a priming mixture of the following composition are prepared:

- 65 gr of damp (24% humidity) diazodinitrophenol, equivalent to 49.5 gr of dry product;
- 39 gr of 99.9% pure commercial stannic oxide SnO₂ supplied by FISA, Pietrasanta (LU);

- 22.5 gr of tetrazene;
- 22.5 gr of calcium silicide with over 65% of the grains below 44 micron and none over 149 micron;
- 7.5 gr of pentaerythritol tetranitrate;
- 7.5 gr of aluminium powder by POMENTON S.p.A. of Venice (average grain size < 100 micron);
- 1.5 gr of gum arabic.

The above products are mixed as follows: the nonexplosive components in the dry state are first mixed together; to this are added the explosive components (DDNP, tetrazene and pentaerythritol tetranitrate) maintained at such a humidity that the final humidity of the mixture ranges between 10 and 15% by weight; the resulting product is metered into primers comprising center-fire percussion caps for NATO 5.56 mm caliber cartridges, each comprising a cap and relative anvil and containing roughly 0.018 gr of the prepared mixture; and the primers are then fitted in known manner to the above cartridges.

Using a damp mixture enables it to be metered more easily into the caps, and provides for maximum safety when preparing and processing the primers.

EXAMPLE 2

The cartridges prepared as in Example 1 were comparison tested with others of the same type featuring traditional primers of the same type but containing a traditional Pb styphnate priming mixture consisting of a commercial product manufactured by the Applicant. Testing comprised an EPVAT and sensitivity test, both performed according to the NATO AC225 standard manual, and the results of which are shown respectively in Tables 1 and 2.

As shown clearly in Tables 1 and 2, the priming mixture prepared as in Example 1 and within the limit values of the invention presents a ballistic efficiency fully comparable with the traditional Pb styphnate mixture. The mixture according to the invention, however, contains absolutely no components currently classed as harmful pollutants, and as such constitutes an effective and, at the same time, truly ecological priming mixture. What is more, the ballistic efficiency of the mixture according to the invention remains high, and within the strict NATO limits governing this type of test, even at low temperature.

The sensitivity test also shows that, though slightly less sensitive as compared with the traditional Pb styphnate mixture, the mixture according to the invention nevertheless still conforms with strict NATO standards as per AC225.

TABLE 1

N° shots + cond.	Ref.	Test cartridges			
		20 + 21°C	30 +21°C	30 +52°C	6 -54°C
Medium Pn (MPa)	340,5	314,2	327,7	280,5	
SD	6,2	4,9			
Medium Pm (MPa)	96,8	93,8	94,9	95,8	
SD	1,261	0,832	0,763		
Medium V24 (m/sec)	915,6	906,8	913,4	878,1	
SD	3,2	3	0,763		
Medium AT (μsec)	1255	1399	1341	1506	
SD	83,5	72,4			
Pn = neck pressure Pm = muzzle pressure V24 = projectile velocity at 24 m AT = action time SD = standard deflection					

TABLE 2

Drop height mm	Primers fired n°	Failed Primers n°
130	0	50
155	1	49
180	13	37
205	31	19
230	38	12
255	47	3
280	49	1
305	50	0
100% failure height = 130 mm H (50% failure) = 203 mm (calculated) S (standard deflection) = 32.44 H+5S = 365.19 (< 450 acceptable) H-2S = 138.12 (> 75 acceptable)		

Claims

1. A priming mixture containing no toxic materials, in particular no Pb, Ba, Sb compounds, and comprising at least one primary explosive; an oxidizing agent; and at least one reducing agent; characterized in that said oxidizing agent comprises stannic oxide SnO_2 .
2. A priming mixture as claimed in Claim 1, characterized in that it also comprises at least one secondary explosive; and at least one friction agent comprising inert abrasive powder.
3. A priming mixture as claimed in Claim 1 or 2, characterized in that it also comprises a binding agent.
4. A priming mixture as claimed in one of the foregoing Claims, characterized in that said oxidizing agent comprises exclusively stannic oxide SnO_2 .
5. A priming mixture as claimed in one of the foregoing Claims, characterized in that it comprises 20 to 60% by weight of primary explosive; 3 to 15% by weight of secondary explosive; 20 to 40% by weight of stannic oxide; 3 to 15% by weight of reducing agents; 5 to 25% by weight of friction agents; and 1 to 5% by weight of binding agent.
6. A priming mixture as claimed in Claim 5, characterized in that said primary explosive is selected from the group comprising diazodinitrophenol, tetrazene, nitromannitol, KDNBF, and mixtures thereof.
7. A priming mixture as claimed in Claim 5 or 6, characterized in that said secondary explosive comprises pentaerythritol tetranitrate.
8. A priming mixture as claimed in any one of the foregoing Claims from 5 to 7, characterized in that said friction agent is selected from the group comprising calcium silicide, silicon monoxide, glass powder, and mixtures thereof.
9. A priming mixture as claimed in any one of the foregoing Claims from 5 to 8, characterized in that said reducing agent is selected from the group comprising aluminium powder, titanium powder, zirconium powder, boron powder, and mixtures thereof.
10. A priming mixture as claimed in any one of the foregoing Claims from 5 to 9, characterized in that said binding agent comprises gum arabic.

11. A percussion primer for center-fire or rimfire percussion cartridges, characterized in that it contains a priming mixture as claimed in any one of the foregoing Claims.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-4 963 201 (R.K. BJERKE ET AL.) * column 2, line 23 - line 39 * * column 3, line 43 - line 59; claim 1 * ---	1,11	C06C7/00 C06B33/00
D,A	EP-A-0 334 725 (NCS PYROTECHNIE ET TECHNOLOGIES) * claim 1 * ---	1,11	
D,A	US-A-4 675 059 (G.C. MEI) * column 2, line 53 - line 58; claim 1 * ---	1,11	
A	GB-A-2 084 984 (CXA LTD./CXA LTEE) * page 1, line 3 - line 6 * * page 1, line 28 - line 30; claim 1 * ---	1,11	
A	US-A-5 145 106 (D.T. MOORE ET AL.) * column 5, line 62 - column 6, line 26; claims 13-16 * ---	1,11	
A	EP-A-0 580 486 (NCS PYROTECHNIE ET TECHNOLOGIES) * claim 1; table 1 * ---	1,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	J. KOHLER ET AL. 'Explosives, Edition 4' 1993, VCH VERLAG, WEINHEIM, DE * page 104 * -----	1,6	C06C C06B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 November 1995	Examiner Schut, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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